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Effect of annealing treatments on the magnetic properties of FeCo/Cu core shell nanostructures

Angshuman Sarkar, Shilabati Hembram, Subhranshu Chatterjee and Amitava Basu Mallick*

Department of Metallurgy and Materials Engineering, Indian Institute of Engineering Science and Technology, Shibpur, Howrah-711103.

Abstract

The core shell structured, soft magnetic materials composed of FeCo core and copper as the shell were synthesized at room temperature electrochemically in an aqueous copper sulfate medium. The morphology, grain size, lattice strain and magnetic properties of the samples were characterized by using atomic force microscopy, x-ray diffraction, and vibrating sample magnetometer. The effect of thermal treatments on the magnetic properties of the FeCo/Cu core shell was studied. It has been found that all the samples are ferromagnetic at room temperature, however, a remarkable improvement in soft magnetic property has been achieved in the sample after compaction and subsequent magnetic annealing. The highest saturation magnetization of 164 emu/g was attained in the magnetically annealed compact sample which is close to the theoretical value of bulk FeCo magnets. The curie temperature of the compact samples was found to be 906°C.

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Keywords: Core shell; FeCo; Magnetic annealing, Saturation magnetization; Curie temperature.

1. Introduction

In recent years, there has been a remarkable increase in interest in the development of nanostructured soft magnetic materials that are both magnetically and electrically conductive, which have potential applications in electromagnetic

* Corresponding author. Tel.: +91-9433739176.
E-mail address: abasumallick@hotmail.com

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shielding, molecular electronics, nonlinear optics, microwave absorption, electric power transmission, transformers, magnetic sensors, electromagnetic noise suppression and automobiles [1-3]. In particular, nanocrystalline soft magnetic materials like Iron, Cobalt, Nickel and their binary and ternary alloys with high saturation magnetization, low coercivity, high permeability and low core loss have been experiencing a rapid improvement over last few decades. In this regard, the binary FeCo alloy has received considerable attention due to their unique magnetic properties, which are sensitive in the micro to nanometer length scale. It is well established that FeCo alloy shows an improved soft magnetic property when the average size of the crystal is smaller than the ferromagnetic exchange correlation length, which is typically in nanometric size range. However, in this size range the soft magnetic property of the FeCo alloy in ambient environment drop sharply due to facile oxidation [4]. Thus, for protection from oxidation, several research efforts have been directed towards applying a coating of stable nonmagnetic layer such as silica, carbon, gold, silver, copper and polymer [5-10] over FeCo nanoparticles to improve their chemical stability. Among these different nonmagnetic coating materials, copper is the most attractive because it provides a good thermal [11] and electrical conductivity [12] to the resultant Cu coated FeCo alloy. However, in earlier reports it is seen that the capping effect of nonmagnetic Cu shell dilutes the soft magnetic property of FeCo core by reducing its saturation magnetization. Hence, it would be worthwhile to mention that compaction and subsequent thermal treatments are the established methods to improve the soft magnetic property by eliminating many structural imperfections from the material. But studies on the effect of different thermal treatments on the magnetic properties of core shell FeCo/Cu nanoparticles is yet to be reported.

Therefore, the present study aims at preparation of FeCo/Cu core shell magnetic nanoparticles by the electrochemical route and investigate their magnetic behaviors as a function of different thermal treatments.

2. Materials and method

The FeCo alloy powder was prepared by wet milling of equiatomic elemental iron and cobalt metal powder [99.9%, Loba Chemie] in a high energy planetary ball mill [P-6, Fritsch] for 35 hours. Toluene [C_7H_8] was used as wet milling medium. The milled powder was dried at 120°C under vacuum for removing residual toluene from the sample. The dried FeCo powder was dispersed in a viscous commercial gum by continuous stirring till the nanoparticles remain in suspended in the viscous medium. 0.1M copper sulfate [$CuSO_4.5H_2O$] aqueous solution was added dropwise to the viscous suspension with continuous stirring till the black suspension yields only characteristic red color of metallic Cu, indicating a Cu coating has been developed over the FeCo powder particles according to the following displacement reaction,

$$M^0 + Cu^{2+} \rightarrow M^{2+} + Cu^0 \quad (1)$$

where, M = Fe, Zn, Al, Co etc.

The final coated powders were collected after washings several times in deionized water. The collected powders were then dried at 120°C under vacuum. A part of the as prepared FeCo/Cu powder was annealed at 600°C for 30 minutes in a furnace, whereas the other part was pressed to make cylindrical compacts under an applied uniaxial load of 625 MPa. The compacts were annealed with and without magnetic field (500 Oe, applied in the direction parallel to applied load) at 600°C for 30 minutes. The designation of the samples that are processed under different conditions are shown in Table 1.

Table 1. Sample identity with respect to processing conditions

	Powder Sample			Compact Sample	
	As milled	As coated	Heat treated	Heat treated	Magnetically heat treated
Sample Id	FC	FCC	H600	CH600	CMH600

The phases present in the samples was identified through x-ray diffraction (XRD) studies using Cu-Kα radiation. The grain size and lattice strain in the sample were analyzed by single line profile analysis (SLPA) of the XRD profiles

[14]. Microstructure and surface topography of the CH600 and CMH600 samples were studied with the aid of atomic force microscopy (AFM) by scanning 2 x 2 μm^2 area of the sample surface in the peak force tapping mode. Magnetic properties of the samples were measured by recording magnetic hysteresis loop at room temperature in a vibrating sample magnetometer (VSM) at a field of 12 KG. The thermomagnetic behaviour of the compact samples was also studied under an applied magnetic field of 10 G from room temperature to 1000°C in VSM.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the of the diffraction pattern of all the samples. The presence of characteristic crystallographic phase of FeCo was evidenced in all the samples. Broadening of the peaks was also observed in both FC and FCC samples, which is attributed to the grain size reduction and lattice strain in the ball milled FeCo. However, in the annealed samples the characteristic peaks of FeCo phase become more prominent, indicating the occurrence of grain growth and reduction of lattice strain. The presence of the characteristic peak of Cu in the coated samples confirms existence of Cu coating over FeCo nanoparticles. The average grain size and lattice strain of the samples, as evaluated from the diffraction pattern of two most intense peaks of Cu (111) and FeCo (110) using SLPA technique are summarized in Table 2.

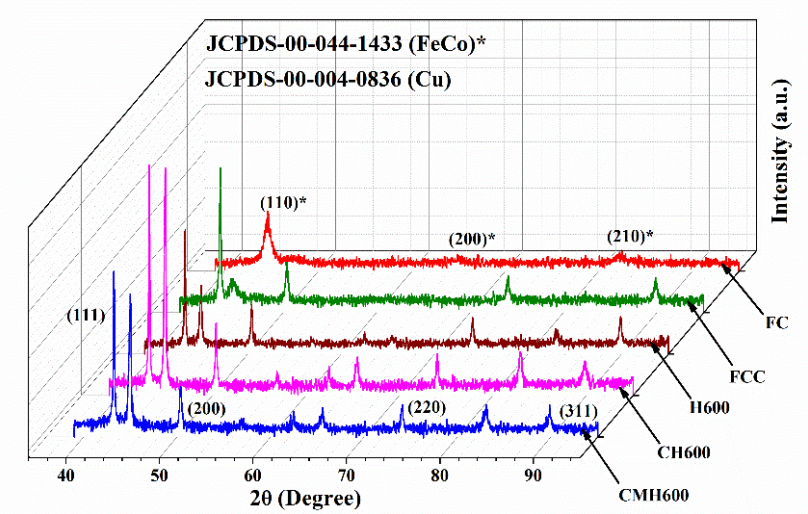

Fig. 1. XRD pattern of the samples.

Table 2. Grain size and lattice strain of the samples calculated using SLPA technique

Sample Id	Grain Size (nm)		Lattice strain (in order of 10^{-3})	
	Core (FeCo)	Shell (Cu)	Core (FeCo)	Shell (Cu)
FC	9.105	--	10.781	--
FCC	9.795	51.947	9.500	2.402
H600	30.310	80.509	3.604	1.842
CH600	49.656	98.011	2.410	1.540
CMH600	33.673	71.928	3.238	1.879

It can be seen from Table 2 that although the grain size and lattice strain values of the as prepared FeCo and Cu coated FeCo/Cu powder are close, on annealing significant increase in grain size of the FeCo core and Cu shell in H600 powder sample occurs with substantial reduction in lattice strain. This has been caused by the annihilation of defect sites generated during processing of FeCo/Cu core shell structure. In the compact samples since the particles are in intimate contact with the surrounding particles condition for grain growth become more favorable when annealed at 600°C. Indeed, this has been reflected in the CH600 compact sample which shows the larger grain size and lower strain compared to the H600 powder sample. Interestingly, in CMH600 compact sample it is seen that the grain growth and the reduction in strain in the material is lower than the CH600. This arises due to the presence of external magnetic field during annealing which causes spin field interaction in the core magnetic atoms, eventually lead to reorganization of lattice atoms and leading anisotropic grain growth in the direction of the applied magnetic field. However, it seems that the short period of thermal treatment is not sufficient to attain complete lattice reorganization and grain coarsening rather the lattice atoms possibly become more disorganized due to the random diffusional motion of atoms towards defect sites for minimization of stored energy leading to generation of high strain in the material.

3.2. Microstructural analysis

The microstructure and topography of the compact CH600 and CMH600 samples were investigated by AFM. Fig. 2 (a) and (c) shows the 2D surface image of the CH600 and CMH600 sample and their corresponding 3D representations are presented in Fig. 3 (a) and (b) respectively. In sample CH600 and CMH600 the average height of the peaks has been found to be 37 nm and 55 nm, respectively, which suggests the presence of the magnetic field during thermal treatment favors directional growth of the particles in CMH600 sample. The average particle size of the samples was estimated by using particle size analyzer software (Nanoscope, Bruker). The histogram profile of the CH600 and CMH600 samples are shown in Fig. 3 (a) and (b) respectively. By best fitting the histogram data using lognormal distribution function [15], the average particle diameter was estimated to be 143 nm and 71 nm for CH600 and CMH600 samples respectively. The small particle size of CMH600 sample compared to the CH600 sample arises due to the two dimensional confined particle growth in CMH600 samples on application of external magnetic field during thermal treatment.

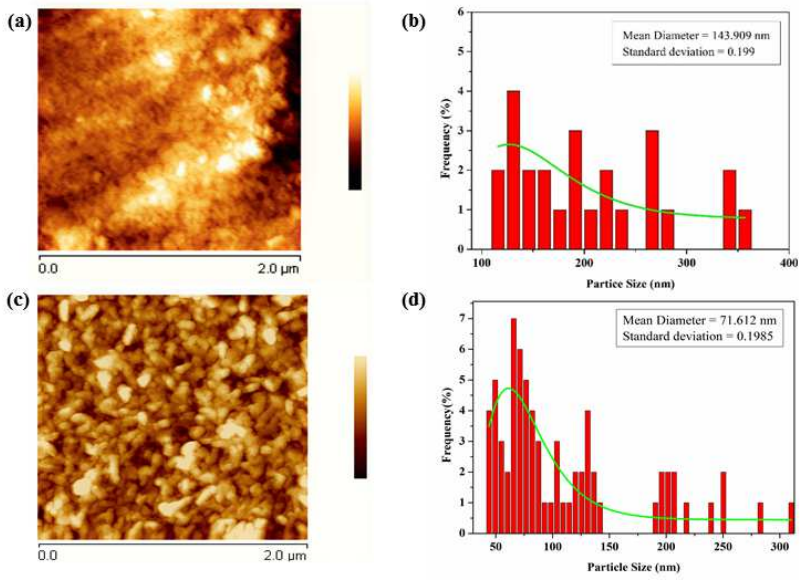

Fig. 2. 2D surface topography of sample (a) CH600 and (c) CMH600. Particle size distribution of sample (b) CH600 and (d) CMH600

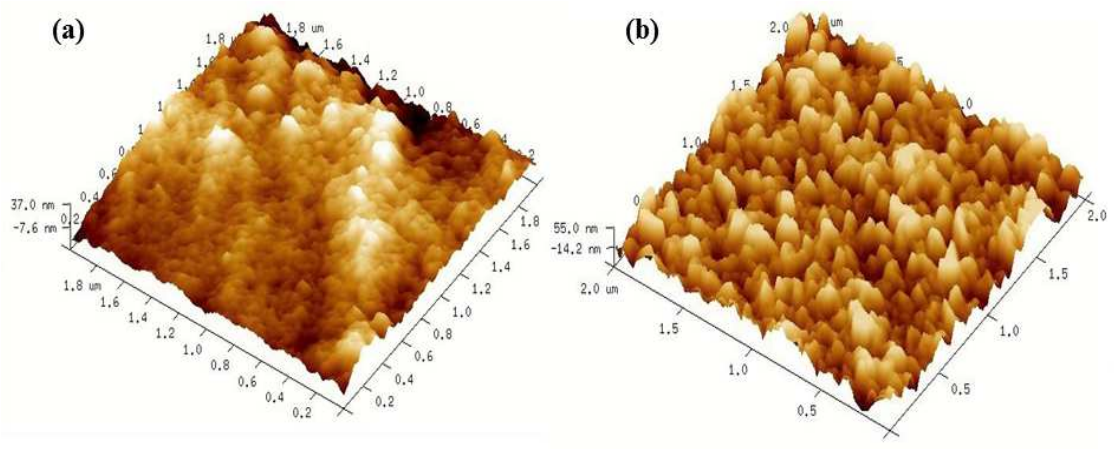

Fig. 3. 3D surface topography of sample (a) CH600 and (b) CMH600

3.3. Magnetic behaviour

Room temperature magnetic hysteresis loops of the samples as represented in Fig. 4 (a) and the inset shows the coercivity (H_c) and remnant magnetization (M_r) values of the samples. The values of the saturation magnetization (M_s) of the materials were determined from the intercepts on the magnetization axis of the M vs. 1/H plot (refer Fig. 4 (b)) [16]. The estimated extrapolated values of the M_s, and H_c for all the powder and compact samples are tabulated in Table 3. It can be seen from the Table 3 that the saturation magnetization in as prepared Cu coated sample (FCC) is considerably low, as the diamagnetic contribution of the thick Cu shell resulted in a low mass fraction of the ferromagnetic core FeCo alloy. However, it was noticed that M_s value has improved significantly in annealed samples and the highest magnetization was recorded for the CMH600 sample, which is slightly lower than the theoretical M_s value of FeCo. This enhancement in magnetization in annealed samples has arisen due to the fact that the annealing treatment provides the low-volume fraction of defects, reduces the strain in the particles and improves the lattice symmetry in the system which favors the formation of magnetic clusters and helped in magnetic domain growth. Moreover, annealing in the presence of an external magnetic field orients the magnetic moments along the applied field direction, which resulted in an increase in the M_s of CMH600 sample to a maximum value of 164 emu/g.

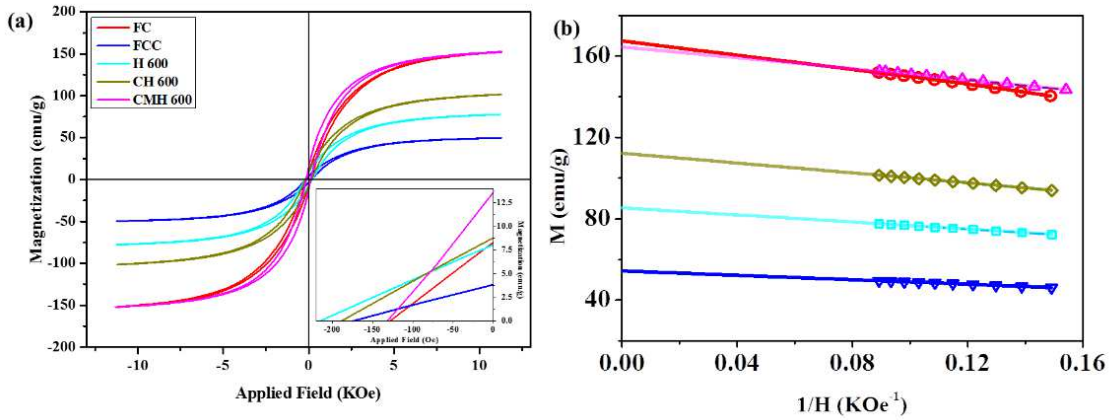

Fig. 4. (a) Magnetic hysteresis loop of the samples. Inset displays the closer view of H_c and M_r and (b) corresponding M vs. 1/H plots.

It can be seen from the Table 3 that the coercivity of the FCC sample is higher in comparison to the ferromagnetic FC sample. This can be attributed to the presence of a diamagnetic Cu shell layer which decrease in the extent of the effective coupling of the dipole moments of ferromagnetic FeCo particles. A sharp drop in coercivty noticed in compact samples (CH600 and CMH600) is caused due to the increase in grain growth kinetics which eases the movement of the magnetic domain walls in the material. However, in annealed powder sample (H600) due to the restriction imposed by the boundary of the individual nanoparticles the movement of the magnetic domain walls is impeded which resulted in the increase in coercivity.

Table 3. Magnetic properties of the samples determined from the hysteresis loop

Sample id	Saturation magnetization (emu/g)	Coercivity (Oe)
FC	167.38	126.53
FCC	54.38	171.32
H600	82.56	215.10
CH600	112.09	186.89
CMH600	164.33	130.95

Thermo-magnetic curves of CH600 and CMH600 compact samples are shown in Fig. 5. It can be seen in Fig. 5 that in the temperature range of 100°-200°C, values of magnetization in CH600 sample increase with temperature and with further increase in temperature, magnetization drops. This can be explained as, on the basis of the fact that with increase in temperature, homogenization of the core FeCo alloy was initiated and possibly undergoes a spinodal decomposition which seems to have led to the formation of few metastable ferromagnetic phases (Fe_xCo_{1-x}) in the system, which resulted in increase in the net magnetization, however with the rise in temperature the metastable phsaes revert back to the parent phase which causes a drop in the magnetization. A sharp rise in magnetization was observed at above 700°C which corresponds to the disorder-order transformation of the FeCo alloy (transition of α´-FeCo to α-FeCo) and above 900°C the magnetization drops to zero due to the ferromagnetic to paramagnetic transformation (transition of α-FeCo to γ-FeCo). Similar phenomena have also been observed in thermo-magnetic plot of the CMH600 sample. However, the magnetization in CMH600 sample was found to be much higher than CH600. This can be attributed to the fact that CMH600 sample attains more ordered structure during annealing in the presence of a magnetic field. The curie temperature of the samples was measured by extrapolation of the curve and was found to be 906°C for both CH600 and CMH600 samples.

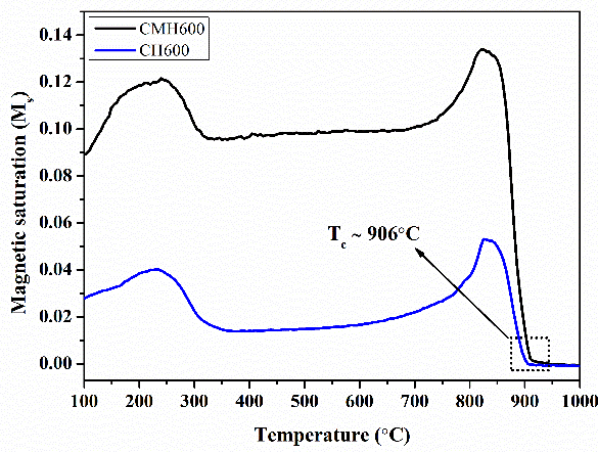

Fig. 5. Thermomagnetic plot of CH600 and CMH600 compact samples.

4. Conclusions

In summary, it can be concluded that FeCo/Cu core shell nanostructure can be successfully prepared by the displacement reaction technique. The XRD results confirm the formation of Cu and FeCo phases in the samples. During thermal treatment of the as prepared sample, grain size increases and lattice strain decreases and these effects are further amplified in heat treated compact sample. However, during annealing of compact samples in the presence of a magnetic field, the grain size reduces with increase in lattice strain. The particle size of the compact heat treated with and without magnetic field samples have been found to be 71 nm and 143 nm, respectively. The saturation magnetization is higher and the coercivity is lower in annealed compact samples than the annealed powder sample due to removal of defects and improvement in lattice symmetry of the material. The highest saturation magnetization of 164 emu/g and the coercivity of 130 Oe were found in magnetically annealed compact sample. It is evident from thermomagnetic analysis that the curie temperature of the compact annealed (with and without magnetic field) samples were found to be 906°C.

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